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Strong kinetic effects on Sr/Ca ratios in the calcitic bivalve

Pecten maximus

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ABSTRACT

Although Sr/Ca ratios in abiogenic calcite are strongly controlled by precipitation rates, such a kinetic effect has never been demonstrated in calcitic bivalve shells. Therefore, we report

Sr/Ca ratios together with daily growth rates in the calcitic shells of 4 individuals of the bivalve *Pecten maximus* (age class I). Ratios of Sr/Ca were found to be variable among individuals that grew at the same location, illustrating that vital effects dominate over environmental controls. Although daily growth rate was correlated with shell Sr/Ca ratios, it explained only half of the Sr/Ca variations. However, daily shell surface area increment, an estimation of the total quantity of carbonate precipitated for a given time, explained 74% of the Sr/Ca variability in the shells of *P. maximus*. This proves, for the first time in a calcitic bivalve, that shell Sr/Ca partitioning is mainly controlled by kinetic effects. The Sr/Ca ratio should therefore be tested as a potential proxy of calcification rate in modern or fossil calcitic biocarbonates.

Keywords: mollusc, calcite, strontium, magnesium, daily growth, temperature proxy.

INTRODUCTION

The Sr/Ca ratio of aragonite skeletons of corals and sclerosponges has proven to be a robust record of past sea-surface temperatures (Weber, 1973; Rosenheim et al., 2004), although some recent studies have stated that kinetic effects can substantially affect strontium partitioning in aragonite (de Villiers et al., 1995; Cohen et al., 2001). Contrary to abiogenic aragonite, experimental studies on abiogenic calcite have demonstrated that Sr/Ca ratios are strongly dependent on precipitation rates (Lorens, 1981; Morse and Bender, 1990; Tesoriero and Pankow, 1996), even if some minor temperature dependence of the Sr incorporation has been reported (Katz et al., 1972). In vivo, kinetic effects have been shown to control Sr/Ca variations in biogenic calcite such as coccoliths and planktonic foraminifera (Lea et al., 1999; Stoll and Schrag, 2000). Nevertheless, a positive temperature influence on Sr incorporation has been observed in coccoliths (Stoll et al., 2002) and foraminifera (Lea et al., 1999), although temperature and growth rate are highly correlated themselves (Stoll et al., 2002). Finally,

solution Sr/Ca ratios and shell Mg/Ca ratios have also been proposed as possible covariables of Sr incorporation in biogenic and abiogenic calcite (Lorens and Bender, 1980; Mucci and Morse, 1983; Carpenter and Lohmann, 1992).

In bivalves, Sr/Ca ratios could potentially be a proxy of temperature, salinity, or Sr/Ca of the water; however, there has been much debate over its meaning (Gillikin et al., 2005). For example, Dodd (1965) found a strong relationship between Sr/Ca in calcite shells and temperature. Later, Klein et al. (1996) suggested metabolic (i.e., metabolic pumping) and/or salinity control on Sr/Ca ratios, whereas Vander Putten et al. (2000) hypothesized kinetic effects. The strong kinetic effects evidenced in abiogenic, foraminiferal, and coccolithophorid calcite have never been demonstrated in bivalve calcite despite numerous studies (Lorens and Bender, 1980; Klein et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003), possibly due to poorly constrained growth rate data, a prerequisite to determine kinetic effects.

In the calcitic bivalve *Pecten maximus*, daily shell growth has been extensively studied over the past ten years, showing temporary shell growth rate reductions uncoupled with temperature or salinity variations (Chauvaud et al., 1998; Lorrain et al., 2000, 2004). This offers the unique opportunity to discriminate environmental (temperature, salinity) versus kinetic controls on Sr/Ca ratios in biogenic calcite.

METHODOLOGY

Living *P. maximus* were collected on 16 September 2003 by dredging at 30 m depth in the Roscanvel bank of the Bay of Brest (France, 4°30'W, 48°20'N). Both temperature and salinity were measured at this site with a Sea-bird 19 CTD (Conductivity, Temperature, Depth) profiler. Seawater Sr/Ca ratios have also been sampled (filtered through 0.4 µm polycarbonate filters and acidified).

Individuals of age class I (showing one winter mark on the shell) with different shell heights (i.e., total dorsoventral length, 6.6, 6.5, 5.6, and 5.5cm for scallops 1, 2, 3, and 4 respectively) were selected for analysis. Scallops of this age have the longest annual growth season and thus accumulate the longest annual calcitic record (Lorrain et al., 2004). Daily growth rate was determined by measuring distances between successive daily growth striae from the winter mark to the shell edge using image analysis (Chauvaud et al., 1998). Absolute dating of each daily growth increment was obtained by backdating growth striae from the collection date. For scallops 3 and 4, growth determination for the first month of spring growth was impossible due to shell surface erosion. Biometric relationships (shell height and shape) used in this paper have been established using more than 1500 individual samples from different European scallop populations.

Using a Merchantek Micromill, carbonate powder was drilled directly from the surface of the left valve of the shells. A 300 μm drill bit was used, which corresponds to a resolution of 1–6 days depending on growth rates. To avoid surface contamination, the surface layer (50 μm depth) of each sample was removed, and the next 100 μm was sampled. These carbonate powders ($\sim 200 \mu\text{g}$) were dissolved in a 1 ml 5% bidistilled HNO_3 solution containing 1 $\mu\text{g l}^{-1}$ of In and Re (internal standards). The Sr/Ca and Mg/Ca ratios of carbonates and seawater were determined using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Finnigan Element2). Reproducibility (relative standard deviation, RSD, $n = 9$) of calcite bivalve shell reference material was 3.4% ($\text{Sr/Ca} = 1.29 \pm 0.04 \text{ mmol mol}^{-1}$) and 3.1% ($\text{Mg/Ca} = 5.89 \pm 0.18 \text{ mmol mol}^{-1}$) for Sr/Ca and Mg/Ca respectively. Reproducibility of a Riverine Water reference sample (National Research Council of Canada SLRS-3), and of an in-house seawater

standard was of 3.5% for Sr/Ca (RSD, $n = 7$), and values were within 3% of recommended values.

Temperature, salinity, and biometric parameters were averaged to the corresponding time sampled from the shell. Statistic treatment was performed by multiple linear regressions.

RESULTS AND DISCUSSION

Substantial interindividual differences were found in the Sr/Ca range and variations (Fig. 1). This suggests a minor involvement of environmental factors on Sr incorporation, since these scallops, sampled at the same location, have all experienced the same environmental conditions. It seems improbable that Sr/Ca ratios of seawater can explain seasonal variations of shell Sr/Ca ratios, as salinity shows little variations over the entire growth season (between 33.5 and 35.5, Fig. 2). In addition to the interindividual differences, all Sr/Ca profiles show an increase during the year and one sharp decrease at the beginning of May (Fig. 1), while temperature and salinity steadily increase between March and September, with no drop in May (Fig. 2). From this, it is clear that the Sr/Ca variability cannot be explained only by temperature or salinity but is mostly controlled by individual biological processes.

Figure 3 clearly shows that Sr/Ca variations are generally well correlated with daily growth. In particular, the decrease of Sr/Ca ratios in the beginning of May is precisely correlated with the reduction in growth during this period in all shells. This growth reduction is a common phenomenon in the Bay of Brest and is related to phytoplanktonic blooms that massively sediment on the bottom (Lorrain et al., 2000). Table 1A lists correlation coefficients (R^2) for the four parameters (growth rates, temperature, salinity, and shell Mg/Ca ratios) and reveals that Sr/Ca ratio variations are indeed better explained by daily growth rates (G) than by the other parameters, with:

$$\text{Sr/Ca (mmol mol}^{-1}\text{)} = 1.364 (\pm 0.057) + 0.002 (\pm 0.0003) * G (\mu\text{m d}^{-1}). \quad (1)$$

When applied to all shells, the model (eq. 1) using only daily growth fits relatively well to the measured Sr/Ca ratios, but some discrepancies remain (Fig. 4). Specifically, predicted values during the summer are lower than expected for scallop 1, whereas they are higher for scallop 3 during the same period. In this sense, the model is not generic; a part of the interindividual variability is not resolved. However, the four individuals have different shell heights, meaning that the total quantity of carbonate precipitated along the growing edge on a given day is different between individuals. Therefore, Sr/Ca ratios are probably more controlled by total CaCO_3 precipitated rather than by linear daily shell growth extension. This quantity can be expressed either by the weight or by the surface of material produced each day. The weight of CaCO_3 produced each day can be calculated using an equation relating shell weight (W in g) and shell height (H in cm) modified from Lorrain et al. (2004) for the same scallop population: $W = 0.195 * H^{2.726}$ ($R^2 = 0.92$, $N = 2419$, $p < 0.0001$). This daily weight increment explains 69.5% of the Sr/Ca variations (Table 1A). Daily shell surface area increment (DSAI) was then estimated using surface area (S in cm^2) and H in cm ($S = 0.802 * H^{2.045}$ ($R^2 = 0.99$, $N = 1707$, $p < 0.0001$)), which itself explains 74% of the Sr/Ca variations (Table 1A). Therefore both estimates of the total quantity of CaCO_3 precipitated provide strong correlations with Sr/Ca ratios. We consider the DSAI as the best explicative variable for Sr/Ca variations, allowing us to establish the predictive model:

$$\text{Sr/Ca (mmol mol}^{-1}\text{)} = 1.464 (\pm 0.027) + 1.552 (\pm 0.155) * \text{DSAI (cm}^2\text{)}. \quad (2)$$

This new model reduces the aforementioned gaps between observed and predicted Sr/Ca ratios (Fig. 4). The addition of temperature or salinity does not improve the model, whereas shell Mg/Ca improves it by only 3.5% (Table 1B). Shell Mg/Ca might explain 3.5% of Sr/Ca

variability by the mechanism proposed by Mucci and Morse (1983), where incorporation of Mg^{2+} causes a distortion of the crystal lattice, leading to the preferential incorporation of Sr^{2+} , a cation larger than Ca^{2+} . However, this would cause a positive linear correlation between Mg and Sr contents, which although significant, is very weak in *P. maximus* (Table 1A). Therefore, Mg/Ca cannot be considered as an important factor for Sr incorporation in these shells. Further addition of temperature and salinity as a third variable is not significant (Table 1C). This result confirms that kinetic effects predominantly control Sr partitioning in the shell of *P. maximus*.

Ratios of Sr/Ca in abiogenic calcite are controlled by precipitation rate, which is a function of seed crystal surface area (Lorens, 1981) and is therefore difficult to estimate in our bivalves without biomineralization experiments. We do not have a measure of these precipitation rates, but our results suggest that daily surface area increments, as a first approximation, seem to be a good reflection of precipitation rates in *P. maximus*. However the model (eq. 2) still leaves 26% of the variance unexplained, suggesting that a better estimation of precipitation rates could be reached. For example, Sr incorporation could depend on the calcification space, i.e., the volume of extrapallial fluid available for calcification. In bivalves, calcification takes place in the extrapallial space (Wheeler, 1992), and we can suppose that the more volume available relative to daily shell production, the more discrimination is possible at biological membranes. Studies on extrapallial fluids would be necessary to go further in this hypothesis. Unexplained remaining variance and interindividual variability in Sr uptake could also come from variations in the microtopographic properties of the calcite crystals, possibly due to changes in the microdistribution, abundance, or composition of the organic matrix (Vander Putten et al., 2000). Indeed, Paquette and Reeder (1995) showed that Sr had largely different distribution coefficients

for different faces in calcite crystals. The overall crystal morphology in these species might differ along the growth axis or between individuals and could explain some of our results.

This study illustrates the importance of having well-constrained growth rates (or calcification rates) when attempting to calibrate proxies in biogenic carbonates. For example, the temperature effect found by Dodd (1965) could be easily explained by the correlation between temperature and growth rates. We also found a significant correlation between Sr/Ca and temperature (Table 1A) but were only able to deconvolve temperature and growth-rate effects because of the growth dip (Fig. 3). The metabolic pumping hypothesis can be also excluded, as high metabolic pumping should result in a decrease of Sr/Ca ratios with an increase in growth rate (see Gillikin et al., 2005), whereas growth and Sr/Ca are positively related in our study (Fig. 3). Finally, salinity does not have an effect on Sr/Ca ratios at the range of 33.5–35.5 (Fig. 2), typical of many shelf areas, but we cannot exclude the effects of large salinity changes such as would be encountered in estuaries.

Mechanisms involved in the kinetic effects may be purely mineralogical, i.e., higher growth rates imply less discrimination against Sr, resulting in a partition coefficient ($D_{Sr} = \text{Sr/Ca}_{\text{calcite}} / \text{Sr/Ca}_{\text{solution}}$) that becomes closer to equilibrium (i.e., $D_{Sr} = 1$). The average shell Sr/Ca ratio was $1.7 \pm 0.1 \text{ mmol mol}^{-1}$ ($n = 144$, Fig. 1), while seawater Sr/Ca had an average value of $8.6 \pm 0.4 \text{ mmol mol}^{-1}$ ($n = 7$). Therefore the mean D_{Sr} is 0.20 ± 0.01 , which is in agreement with other biogenic and abiogenic calcites (Lorens and Bender, 1980; Carpenter and Lohmann, 1992). It is also interesting that *P. maximus* D_{Sr} values are similar to that of other calcitic organisms such as coccoliths (Stoll et al., 2002) and foraminifera (Lea et al., 1999), which have very different biomineralization mechanisms. This could suggest that shell Sr/Ca ratios are independent of these biomineralization mechanisms. However, this is not the case for

all trace elements, as Mg/Ca ratios are well correlated with temperature in coccoliths and foraminifera (Lea et al., 1999; Stoll et al., 2001), while we do not find any correlation in *P. maximus* ($R^2 = 0.03$).

CONCLUSIONS

Daily surface area increments explain much of the observed shell Sr/Ca variations in *P. maximus*. Further studies on bivalves should therefore consider this when attempting to reconstruct environmental parameters from shell Sr/Ca ratios. Estimation of daily surface area increments could be performed in other species to see if this model can be extended to other biomineralizing organisms such as coccoliths and foraminifera. Indeed, if the link between calcite precipitation and Sr/Ca ratios is better constrained for more species, Sr/Ca might be a useful proxy of calcification rates. This would be extremely useful for modern and fossil species in which daily growth cannot be easily measured.

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Table 1: Statistical results (N = 144) of the linear regressions between shell Sr/Ca ratios and possible dependent variables. (A) Simple regression between Sr/Ca and different dependent variables. (B) Multiple regression using DSAI (daily surface area increment) as the first dependent variable. (C) Multiple regression using DSAI and Mg/Ca as the two first dependent variables. R^2 refers to the correlation coefficient.

				Overall significance	Significance of additional variables	
A	Variables			R ²		
	DSAI			0.74	P <0.01	
	Daily Weight Increment			0.7	P <0.01	
	Daily Growth Rate			0.52	P <0.01	
	Temperature			0.49	P <0.01	
	Salinity			0.49	P <0.01	
Mg/Ca			0.28	P <0.01		
B	1 st variable	2 nd variable			Significance of 2 nd variable	
	DSAI	Temperature		0.74	P <0.01	P = 0.8170
		Salinity		0.74	P <0.01	P = 0.3644
		Mg/Ca		0.78	P <0.01	P<0.001
C	1 st variable	2 nd variable	3 rd variable		Significance of 3 rd variable	
	DSAI	Mg/Ca	Temperature	0.78	P <0.01	P = 0.3113
			Salinity	0.77	P <0.01	P = 0.7723

FIGURE CAPTIONS

Figure 1. Ratios of Sr/Ca (black symbols) and Mg/Ca (gray symbols) (mmol mol^{-1}) in the calcite shell layer of four *P. maximus* specimens (age class I) sampled in September 2003 in the Bay of Brest. Error bars represent analytical reproducibility (1σ).

Figure 2. Bottom (30 m) seawater salinity and temperature ($^{\circ}\text{C}$) variations for the year 2003 in the Bay of Brest.

Figure 3. Daily growth increments (gray symbols, $\mu\text{m d}^{-1}$) and shell Sr/Ca ratios (black symbols, mmol mol^{-1}) in 2003 for the four age class I *P. maximus* specimens of the Bay of Brest.

Figure 4. Modeled shell Sr/Ca ratios calculated from daily growth (eq. 1, white symbols) and daily surface area increment (eq. 2, gray symbols) for the four scallops in 2003. Measured shell Sr/Ca ratios (mmol mol^{-1}) are shown as black symbols.







